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THE SURFACE TENSIONS OF MOLTEN GLASS

BY

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ENGINEERING EXPERIMENT STATION
BULLETIN SERIES No. 311

THE SURFACE TENSIONS OF
MOLTEN GLASS

PART I
SURFACE TENSIONS OF MOLTEN GLASSES

BY
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PART II
SURFACE TENSIONS OF SODA-LIME-SILICA MELTS

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THE SURFACE TENSIONS OF MOLTEN GLASS

I. INTRODUCTION

1. *General Introduction.*—Surface tension data pertaining to molten glass are singularly lacking, notwithstanding their very great importance. The explanation seems to be found chiefly in two facts: first, the special apparatus required is costly, and the technique necessary for investigations conducted at high temperatures is difficult, since it involves the close control and measurement of these temperatures; second, until very recently, glass technology had not received the attention it deserves because of the lack of research laboratories properly equipped and staffed for such investigations.

With the rapid introduction of newer and better methods of manufacture of glassware such as the "gob" feeders, the tube drawing process, the Corning bulb machine, the continuous drawing of flat glass, etc., the importance of a better knowledge and control of the viscosity and surface tension of molten glass has received wider recognition.

The surface tension of molten glass is of prime importance in practically all operations of manufacturing glass wares, beginning with the fining process, and continuing until the glass becomes rigid. It is probably a factor associated with the durability of surfaces exposed to weathering. When glass wares are formed in molds, smooth surfaces are desired, excepting as modified by details of the design; in any case, the phenomenon of surface tension is involved.

Surface tension is probably a function of molecular and ionic attraction and its measurement has been found useful in studying the molecular states in liquids.

2. *Work of Previous Investigators.*—There have been a number of attempts to measure the surface tensions of glasses and other liquids at elevated temperatures. Tillotson* measured the surface tensions of a series of commercial glasses above their softening temperatures by weighing the drops which fell from the end of a glass fiber as it was fed into the flame of a blast lamp. The results were expressed in dynes per centimeter, and were said to be reproducible when similar conditions were used. The author did not claim to have obtained absolute values.

Griffith† used the Quincke drop-shape method to determine the surface tension of a glass at 1100 deg. C. At lower temperatures, he

*Tillotson, E. W. "Surface Tensions of Molten Glasses" Jour. Ind. Eng. Chem. Vol. 3, 631, 1911; 4, 651, 1912.

†Griffith, A. A. "The Phenomena of Rupture and Flow in Solids" Phil. Trans. Roy. Soc. Lon. Series A, Vol. 221, 163, 1920.

determined the surface tension from the amount of sagging in a fiber supported at its ends and loaded centrally. The values indicated that the surface tension of the glass was slightly higher than 400 dynes per centimeter in the temperature range 745 to 1100 deg. C.

Washburn and Libman* determined the surface tensions of a number of soda-lime-silica glasses at 1206 deg. C. and 1454 deg. C. by measuring the amount of force required to free a cylinder from contact with the surface of molten glass. The values were of the order of 150 dynes per centimeter.

Lecrenier† employed a drop-weight method to find the surface tensions of a number of different glasses. The values obtained varied between 410 and 480 dynes per centimeter at 1050 deg. C. and 1150 deg. C. The effect of many different oxides on the surface tension was shown.

Recent work by Pietenpol and Scott‡ on the surface tensions of commercial glasses yielded values in the region of 230 to 360 dynes per centimeter. The temperatures used depended somewhat on the glass being studied, but were included in the range of 550 deg. to 900 deg. C. The method used in making the measurements was called the "bulb" method by the authors.

Lecrenier§ referred to some work by Quincke on the surface tensions of glasses, but no other reference has been found.

The effect of additions to soda-lime-silica glasses of small amounts of volatile salts has been studied.¶ While surface tension was one of the properties investigated, the method of measurement was not mentioned in the abstract of the work which was available.

Jaeger** measured the surface tensions of molten salts to 1650 deg. C. by use of the Maximum Bubble-Pressure method. The results of his careful work are generally accepted as being correct.

3. Maximum Bubble-Pressure (Jaeger) Method for Determining Surface Tension.—It is a frequent observation that most liquids show "capillary rise" in small tubes which are brought into contact with their surfaces. If the other influencing factors are held constant, the rise in the small tube is proportional to the surface tension of the

*Washburn, E. W., Shelton, G. R. and Libman, E. E. "The Viscosities and Surface Tensions of the Soda-Lime-Silica Glasses at High Temperatures" Univ. of Ill. Eng. Exp. Sta. Bul. 140, 1924.

†Lecrenier, A. "Mesure de la Tension Superficielle du Verre" Bull. Soc. Chim. Belg. Vol. 33, 199, 1924, and Vol. 34, 27, 1927.

‡Pietenpol, W. B. and Scott, H. H. "The Surface Tension of Molten Glass." Physics Vol. 7, 26, 1936.

§Lecrenier, A.; see above.

¶Vickers, A. E. J., Sugden, J. A., and Bell, R. A. "Effect on Viscosity and Surface Tension of Molten Soda-Lime-Silica Glass of the Addition of Small Amounts of Volatile Salts." Abstracted: Atti I^o Congr. internat. vetro e ceram. pg. 679, 1933. Ceramic Abstracts Vol. 14, 212, 1935.

**Jaeger, F. M. "Über die Temperaturabhängigkeit der molekularen freien Oberflächenergie von Flüssigkeiten." Zeitschr. anorg. u. allgem. Chemie Vol. 101, 1, 1917. "Optical Activity and High Temperature Measurements," New York, 1930.

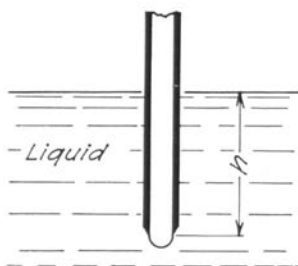


FIG. 1. ILLUSTRATION OF MAXIMUM BUBBLE-PRESSURE METHOD FOR MEASURING SURFACE TENSION

liquid. When the weight represented by the rise of the liquid is divided by the circumference of the inside of the tube, the quotient gives an approximate value for the surface tension of the liquid. If pressure be applied to force the liquid downward until its surface reaches the lower opening of the capillary, then the pressure will be equivalent to that exerted by the column of the liquid displaced. If capillary rise may be taken as a function of surface tension, then the pressure necessary to prevent capillary rise is also a measure of surface tension.

To take another view of the maximum bubble-pressure method of measuring surface tension, suppose a bubble to be blown on the end of a tube dipping vertically into a liquid to a depth h , as indicated in Fig. 1. As the bubble is being formed, the gas pressure in it may be increased until the point of least radius of curvature is reached. With small tubes, the bubble approaches a hemisphere with a radius the same as that of the tube at the instant of least radius. As the pressure is increased further, the bubble must expand. This expansion increases the radius of curvature, and the pressure which is in the bubble is at once excessive so that a further expansion occurs and leads to bursting.

The pressure in a bubble which is formed below a liquid surface may be attributed to (1) hydrostatic pressure, and (2) surface tension effects. If the depth of immersion of the tube and the density of the liquid are known, the calculation of the first is simple. As for the second, the force exerted by surface tension along any great circle is equal to $2\pi rT$, where r is the radius and T is the surface tension. This force is distributed over the area of the great circle, which is πr^2 , and thus the pressure due to surface tension

is $2 \frac{T}{r}$.

The Schrödinger* approximation has been used in relating experimental observations to calculated values of surface tension.

This equation has the form:

$$T = \frac{\bar{p}r}{2} \left(1 - \frac{2r}{3h} - \frac{1r^2}{6h^2} - \dots \right) \quad (1)$$

where T = surface tension in dynes per centimeter

\bar{p} = (total pressure - hydrostatic pressure) on bubble in dynes

r = the radius of the tip of the tube in centimeters

h = the height of a column of test liquid equivalent to \bar{p} in centimeters

(The term $\frac{1r^2}{6h^2}$ may be neglected in most cases.)

It is possible to derive the equation by assuming a hemispherical bubble being blown at the end of the tube. (The Schrödinger approximation is applicable to small tubes and bubbles which are approximately hemispherical.) In addition to the symbols introduced above, the following are used:

p = the total pressure in the bubble minus the hydrostatic pressure in grams per square centimeter

d = the density of the liquid in grams per cubic centimeter

g = the gravity constant

$$2\pi rT = (p\pi r^2 - \frac{2}{3}\pi r^3d), \text{ or}$$

the force of surface tension is equal to the total pressure in the bubble minus the buoyant force of the hemisphere.

Transposing,

$$\frac{T}{g} = \frac{pr}{2} \left(1 - \frac{2rd}{3p} \right)$$

The height of liquid equivalent to p is

$$h = \frac{p}{d}$$

*Schrödinger, E. "Notiz Über den Kapillardruck im Glasblasen." Ann. Physik 47:46, 413-418, 1915.

then,

$$\frac{T}{g} = \frac{pr}{2} \left(1 - \frac{2r}{3h} \right)$$

but

$$pg = \bar{p} \text{ of Equation (1)}$$

and hence

$$T = \frac{\bar{p}r}{2} \left(1 - \frac{2r}{3h} \right)$$

Sugden* has prepared a table of values for making corrections in cases where larger tubes are employed and the bubble becomes appreciably flattened. A calculation of some of the data from this report indicated that the difference between the results obtained by the use of Sugden method and those obtained by the Schrödinger approximation was negligible.

Jaeger† has also suggested a correction for maximum bubble-pressure measurements of surface tension. In this instance, the molecular weight of the liquid in question must be known. Obviously such a correction could not be used with glasses where the molecular state is very uncertain.

The history of the maximum bubble-pressure method of measuring surface tension has been ably presented by Sugden‡ and Adam.§ Dorsey¶ also discusses the method.

The maximum bubble-pressure method is alternatively known as the "Jaeger" method, because F. M. Jaeger was active in developing the method and in applying it to many different liquids.

4. *Purpose of This Bulletin.*—This bulletin was written for the purpose of describing a method for the measurement of the surface tension of molten glasses and presenting the results of those measurements, since it was realized that reliable data on surface tension of glasses were needed. At the time that the experimental work was undertaken, various authors had reported widely different results from their individual measurements, and therefore it seemed desirable to employ a reliable method not previously used. It was expected that the results of the present measurements might confirm

*Sugden, S., "The Determination of Surface Tension from Maximum Pressure in Bubbles: II," Jour. Chem. Soc. (London), Vol. 124, 27, 1924.

†Jaeger, F. M., loc. cit.

‡Sugden, S., "The Determination of Surface Tension from Maximum Pressure in Bubbles, I," Jour. Chem. Soc. (London), Vol. 121, 853, 1922.

§Adam, N. K., "The Physics and Chemistry of Surfaces," Oxford, 1930.

¶Dorsey, N. E., "Measurement of Surface Tension," Bur. of Stds. Scientific Paper No. 540. Washington, 1926.

TABLE 1
COMPOSITIONS OF EXPERIMENTAL SODIUM BOROSILICATE GLASSES

Sample No.	Percentage Composition				
	SiO ₂	Na ₂ O	B ₂ O ₃	R ₂ O ₃	Total
1	59.83	27.05	56.99	4.70	98.57
2	71.73	20.36	3.84	3.88	99.39
3	54.91	21.91	18.64	2.02	97.48
4	64.86	18.56	12.96	1.56	97.94
5	74.12	13.38	11.00	1.26	99.76
6	58.96	14.61	22.72	2.12	98.41
7	69.14	10.24	17.48	1.88	98.74

The "R₂O₃" was probably introduced in the preliminary melting of the glasses.

those from some other independent investigation in the general study of silicate glasses.

5. Acknowledgment.—

This investigation has been a part of the work of the Engineering Experiment Station, of which Dean M. L. Enger is the director, and of the Department of Ceramic Engineering, of which Prof. Cullen W. Parmelee is the head.

The initial work was done by K. C. LYON as Research Graduate Assistant of the Engineering Experiment Station and is reported in Part I; the data reported in Part II was obtained by C. G. HARMAN.

II. MEASUREMENT OF SURFACE TENSIONS OF MOLTEN SODA-BORIC OXIDE-SILICA GLASSES

6. *Compositions of the Glasses.*—Seven glasses were prepared in order to study the surface tension of molten sodium borosilicate mixtures. The raw materials from which the glasses were prepared were proportioned to yield compositions within the limits of

10 to 30 per cent Na₂O

10 to 25 per cent B₂O₃

55 to 75 per cent SiO₂

The chemical analyses of the fused glasses as used were found* to be as given in Table 1.

These glasses were chosen for testing because they could be melted easily, and because they had comparatively low viscosities in the molten condition. The compositions include some simple vitreous enamel frits.

*J. M. Lindgren, analyst.

7. *Apparatus.*—The apparatus used in measuring the surface tensions of the glasses was designed after a number of preliminary studies of the method and its requirements. These studies included measurements of surface tensions at room temperature, and at higher temperatures. A glass capillary was used for such liquids as water, alcohol, and anilin. A sillimanite tube of small bore was used for making measurements with molten salts and a molten vitreous enamel. While the tube was corroded by the melts at higher temperatures, the measurements made with it were useful in the later design of equipment.

The apparatus used is shown schematically in Fig. 2a, and details of certain parts are given in Figs. 2b, 2c, and 3. A photographic view of the apparatus is shown in Fig. 4.

The apparatus shown in Fig. 2a was connected to the laboratory compressed air supply. The supply pressure was 50 lb. per sq. in., which was reduced to 10 lb. per sq. in. by means of a reducing valve. The needle control valve was used in controlling the pressure in the apparatus. The drying cylinder, 7 cm. in diameter and 85 cm. in length, was filled with calcium chloride grains. The flow gauge was used only qualitatively. The manometer gauge was built from selected glass tubing of 0.595 ± 0.009 cm. internal diameter. The construction of the manometer is shown in Fig. 2b. The meniscus was illuminated through the translucent screen from the rear and was viewed through the telescope of the cathetometer. Readings of liquid level were made on the scale, which was attached to the side of the manometer tube. Both the manometer and the flow gauge were filled with *n*-dibutyl phthalate whose density is slightly greater than that of water and whose surface tension is of the order of 33 dynes per cm. at 26 deg. C.

It will be seen that the box containing the manometer, Fig. 2b, and all of the exposed parts of the apparatus conveying the air current were covered with felt because it was necessary to maintain the system at a constant temperature in order to make a satisfactory measurement. As will be explained later, the pressure in the system had to be held constant during a part of the measuring period, and therefore, it was necessary to maintain a constant temperature during this period.

The parts of the apparatus were connected by glass tubing of 8 mm. internal diameter. Where lengths of glass tubing had to be joined with rubber tubing the joints were as short as possible, and were made gas-tight with wax.

The capillary tube was made from an alloy of 60 per cent platinum

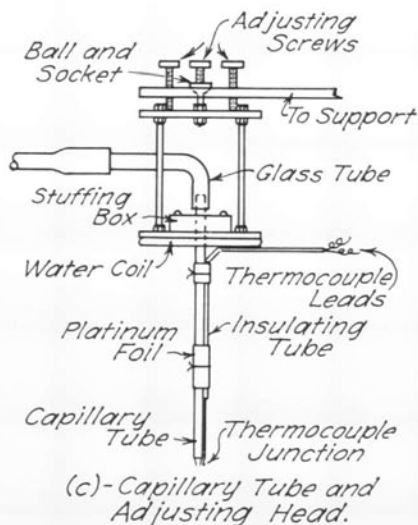
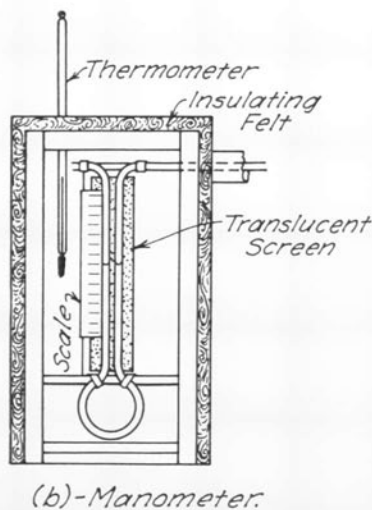
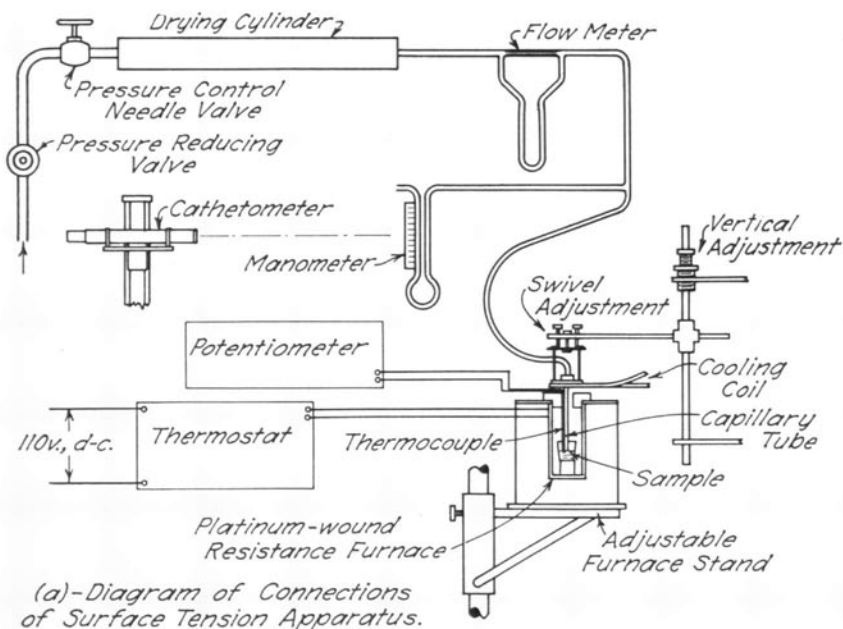


FIG. 2. SCHEMATIC DIAGRAM OF SURFACE TENSION APPARATUS

and 40 per cent rhodium, which was chosen because of its rigidity. It was 14 cm. in length and had an outside diameter of 0.4 cm. The internal diameter of 0.3 cm. was decreased to 0.13 cm. at a point one centimeter from the lower tip. The tip end was tapered at an

angle of approximately 30 deg. to the tube axis to leave a narrow lip. A piece of glass tubing was fused on the upper end of the capillary, and this was connected with the system by a rubber tube 40 cm. in length. The capillary tube and its holder are shown in Fig. 2c. The tube was wrapped with asbestos string and held by pressure in the stuffing box so that there was no metallic contact between the tube and the holder. The adjustment of the swivel head permitted the tube to be swung into a vertical position by manipulation of the screws. The water cooling coil served to protect the mounting from the heat of the furnace.

As shown in Fig. 2a, the swivel head was supported in such a way that it could be moved vertically by a screw adjustment. The support and screw adjustment were fastened to a rigid iron framework which was clamped firmly to the laboratory table.

The sample, in a platinum crucible of 25 cc. capacity, was placed in an electrically-heated resistance furnace 5 cm. in internal diameter. It was closed by a piece of "Sil-o-cel" material of 2.5 cm. thickness cut to give a close fit and pierced with a hole to permit the entrance of the capillary tube. The furnace was set on a counter-weighted platform which could be adjusted to any desired level.

The temperature of the sample was determined by placing the junction of a platinum-platinum-rhodium thermocouple in close proximity with the top of the capillary tube, but above the end of the same. The thermocouple was connected to a portable potentiometer by compensating lead wires.

The thermocouple was corrected by calibration against another couple which had been standardized. The melting points of aluminum, copper, sodium chloride, and ice were used for standardizing. The readings of the portable potentiometer were compared with the readings of a Leeds and Northrup Type K potentiometer.

The furnace temperature was held nearly constant* by the use of a thermostat the arrangement of which is shown in Fig. 3. A similar instrument has been described by Bunting† and by Roberts.‡ The thermostat operated to keep the resistance of the furnace constant. The platinum windings of the furnace underwent a greater change in resistance with change of temperature than did the resistances (Chromel) of the rest of the thermostat circuit. The relation of resistance to temperature provided a convenient means for temperature regulation.

*Variations in temperature could not be observed with the pyrometry equipment.

†Bunting, E. N. "An Electric Furnace Temperature Regulator," *Jour. Amer. Ceram. Soc.* Vol. 6, 1209, 1923.

‡Roberts, H. S. "The Geophysical Laboratory Furnace Thermostat," *Geophysical Laboratory Paper No. 573*, 1925.

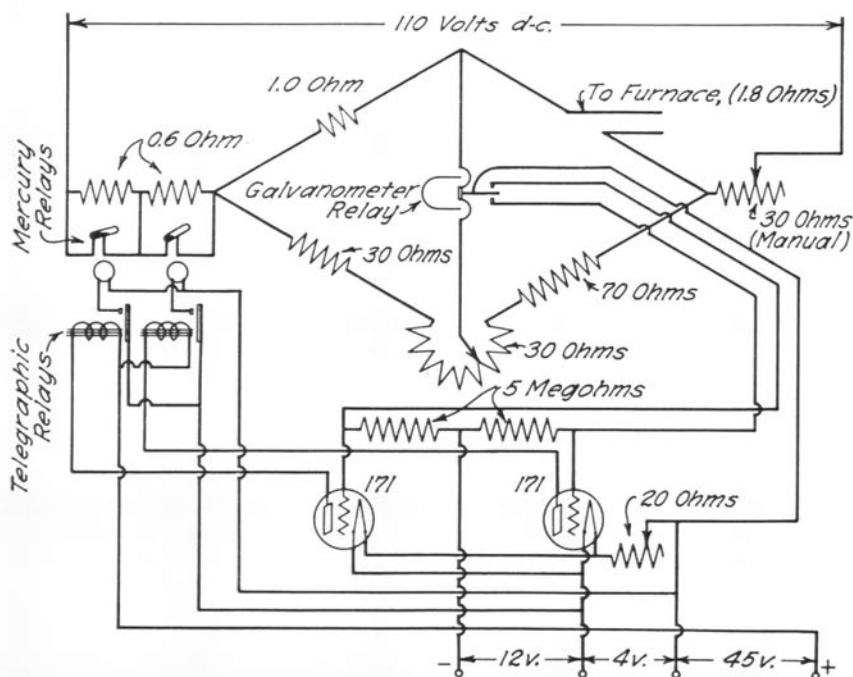


FIG. 3. ELECTRICAL DIAGRAM OF THERMOSTAT

Figure 4 shows the apparatus as it was arranged for measuring the densities of the molten glasses; these data were needed for correction in calculating the surface tension. The apparatus consisted of a platinum ball of 0.55 cc. volume suspended in the melted glass in the furnace from the beam of the balance shown in the figure. An extension member included in the suspension permitted adjustment of the depth of the immersion of the ball in the glass. The temperature of the sample was found by immersing a platinum-platinum-rhodium thermocouple in the melt near the platinum ball.

8. *Preparation of Samples.*—The glass samples used in this determination were prepared by melting:

Raw Material	Chemical Formula Assumed
Soda ash	Na_2CO_3
Ottawa quartz	SiO_2
Pacific Coast borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot n\text{H}_2\text{O}^*$

*"n" was determined by loss of weight in fusion and by titration.

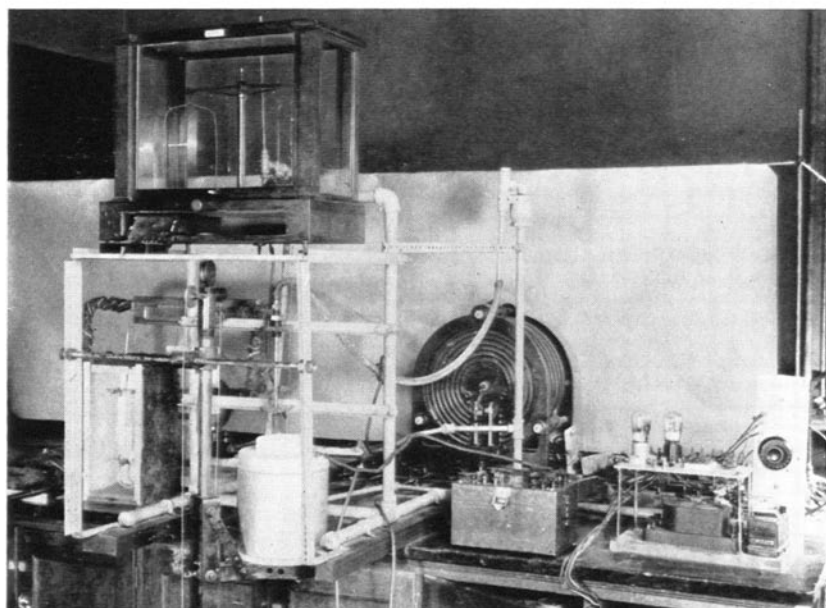


FIG. 4. ARRANGEMENT OF APPARATUS FOR DENSITY DETERMINATIONS

TABLE 2
CALCULATED COMPOSITIONS OF EXPERIMENTAL GLASSES

Glass No.	Percentage by Weight		
	Na ₂ O	B ₂ O ₃	SiO ₂
1	30	10	60
2	25	5	70
3	25	20	55
4	20	15	65
5	15	10	75
6	15	25	60
7	10	20	70

These materials were proportioned to yield melts of the calculated compositions shown in Table 2.

The compositions are from a field studied by Andrews* in developing acid-resistant vitreous enamels.

Three kilograms of each glass batch were prepared by mixing the raw materials by passing them three times through a sieve having twenty meshes to the inch and then rolling them on paper after each

*"Acid Resisting Cover Enamels for Sheet Iron." Univ. of Ill. Eng. Exp. Sta. Bul. No. 201, 1930.

sieving. The glasses were melted in fire-clay crucibles in gas-fired furnaces at an average temperature of 1100 deg. C. When the glasses had melted down, they were stirred with a rod of illium alloy and then were poured into distilled water. The water was removed from the samples as soon as possible, and they were dried in a steam-heated drier.

After the glasses had dried, they were placed in porcelain ball mills and ground to pass through a twenty-mesh (to the inch) sieve. Each glass powder was mixed on paper and again melted in a fire-clay crucible at a temperature near 1100 deg. C. in a large electric resistance furnace. The stirring, quenching, and grinding processes were repeated, and the resulting glass powders were used for samples in the determination of surface tension and density.

The analyses of the fused glass samples have already been given in Table 1.

9. *Experimental Procedure.*—To make a determination of surface tension, a sample of powdered glass was placed in a platinum crucible and heated in the resistance furnace to a temperature slightly above 1250 deg. C. The thermostat was adjusted to maintain this temperature.

The capillary tube was mounted beneath a microscope and its diameter at the tip was measured in four directions. The average of these measurements was taken as the diameter of the capillary opening.* The orifice was examined critically at the time of measurement. If there was a difference of more than 0.5 per cent between the greatest and least diameter, the opening was worked to make it more nearly circular.

In order to insure placing the major axis of the capillary at right angles to the plane of the surface of the melt, a glass microscope slide was placed in contact with its opening and fastened there with wax. The tube was then mounted above the furnace, and the holder adjusted to bring the glass slide parallel to and in contact with a free mercury surface in a small dish. Any deviation of the capillary tube from a true vertical position was immediately apparent. This adjustment assured that the tube was in proper position for making the measurements of surface tension. When the tube had been adjusted, the dish of mercury was removed, the glass slide was freed by melting the wax, and the furnace was raised to bring the tube in contact with the surface of the molten glass.

*Under the influence of contact with the molten glass, the metal of the capillary became slightly roughened, and it was necessary to polish the capillary tip from time to time. This was done with a piece of soft paper or, in rare cases, rouge.

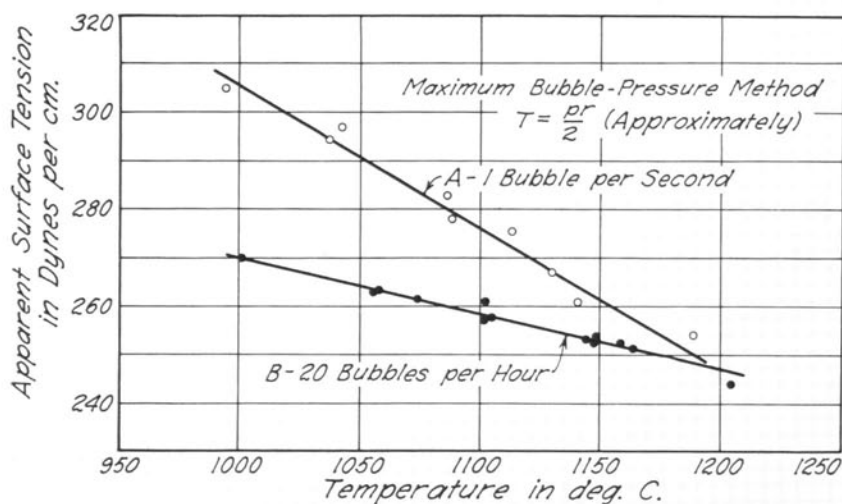


FIG. 5. EFFECT OF RATE OF BUBBLE FORMATION UPON APPARENT SURFACE TENSION OF A GLASS

The contact of the capillary tube with the molten glass suddenly stopped the slight flow of air, and this was immediately shown by the flow gauge. This method of locating the surface with respect to the tube had been recommended by Jaeger,* and was found to be satisfactory.

The furnace was raised by hand to bring the sample into contact with the capillary tube. Since this necessarily gave a crude adjustment, the tube was raised slightly by the vertical adjustment, and lowered again to touch the surface.

After the tube had been placed in contact with the surface, the pressure in the system was allowed to increase slowly until a bubble had formed and burst. After one bubble had burst, the next was allowed to form more slowly, and the pressure was held at a point somewhat less than that found necessary for breaking the preceding bubble. This manipulation was repeated until a pressure was found which could be maintained for at least two minutes before bursting the bubble, and which would burst the bubble in something less than ten minutes. The system had to be gas-tight to permit holding the pressure constant.

The effect of rate of formation and bursting of the bubble is clearly shown in the curves of Fig. 5.

The pressure of the air in the apparatus was controlled by manip-

*Jaeger, F. M., loc. cit.

ulation of the needle valve. The pressure in the bubble was found by taking readings of the meniscus levels on the scale of the manometer by use of the cathetometer. Both the upper and the lower levels could be read during the constant pressure period. The scale was divided into 0.5 mm. divisions, and readings were estimated to 0.1 mm.

After the pressure necessary to burst a bubble at any one temperature had been found, and had been checked by repetition, the capillary tube was removed from the melt, and the thermostat was adjusted to bring the furnace to some other temperature for new readings.

It is to be noted that the procedure used in this series of determinations was modified from Jaeger's procedure in that the tip of the capillary was placed at the surface of the liquid and was not immersed to some depth. This change in procedure eliminated the necessity for a careful measurement of the depth of immersion of the tube, and removed the need for an accurate determination of the density of the sample. (When density data are needed only for calculation of " h " of the Schrödinger approximation, their precision need not be great for tubes of small diameter.)

This new procedure was used for measuring the surface tension of water at room temperature and the surface temperature of sodium chloride at temperatures near 900 deg. C. The results obtained were as follows:

Surface tension of distilled water at 24 deg. C.

Experimental value.....	72.2 dynes per cm.
Value from international critical tables.....	72.13 \pm 0.05 dynes per cm.

Surface tension of sodium chloride

Temperature—deg. C.....	849	885	930
Experimental value—dynes per cm. (air).....	111.6	108.4	105.3
Value from international critical tables—(inter- polated) dynes per cm. (nitrogen).....	110.5	107.8	104.6

The results of these measurements indicated that the procedure adopted, namely, that of placing the capillary tip in contact with the surface without immersion, yielded values which compared favorably with approved data.

Although Jaeger* had reported success in measuring the surface tensions of liquids of appreciable viscosity by use of the maximum bubble-pressure method, it was anticipated that there might be some criticism of its application to the measurement of viscous

*Jaeger, F. M., loc. cit.

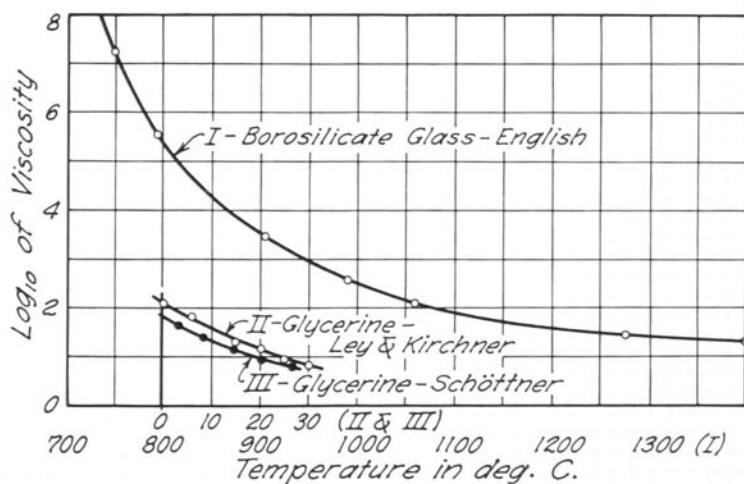


FIG. 6. VISCOSITIES OF GLASS AND GLYCERINE

glasses. English* has measured the viscosity of a glass of the composition:

	per cent
Na ₂ O.....	19.95
B ₂ O ₃	14.45
SiO ₂	64.72
Minors.....	0.92

This glass approached our No. 4 in composition. The results of the measurements of viscosity of this glass are given graphically in Fig. 6. The results of measurements of the viscosity of glycerine by Ley and Kirchner† and by Schöttner‡ are also given in Fig. 5. It may be seen that the viscosity of glycerine at temperatures near 0 deg. C. approaches the viscosity of the glass in the region near 1100 deg. C. Some experimental measurements of the surface tension of glycerine were made with the apparatus. The same technique was used in making the measurements of the surface tension of glycerine as was used in making measurements of the surface tension of molten glass. The results of the measurements

*English, S. "The Effect of Composition on the Viscosity of Glass." Jour. Soc. Glass Tech. Vol. 8, 205, 1924.

†Ley, H. and Kirchner, U., "Über die innere Reibung hochviscöser Stoffe," Zeit. f. anorg. u. alg. Chem., Vol. 173, 395, 1928.

‡Schöttner, Franz, "Über die Ermittlung des Coefficienten der Innern Reibung in Zähnen Flüssigkeiten, durch Fallversuche," Wien, Ber., 77, Part 2, p. 682, 1878, and 79, Part 2, p. 477, 1879.

compared with values obtained by interpolating and extrapolating International Critical Table data as follows:

Surface tension of glycerine

Temperature—deg. C.....	25.5	2.0
Experimental value*—dynes per cm. (air).....	62.9	64.7
International critical table value†—dynes per cm. (air).....	62.0	64.4

It can be seen from these values that it was possible to get satisfactory results within the limits stated when the surface tension of a viscous substance was measured by the maximum bubble-pressure method.

In order to determine the density of a glass, the sample was heated in a platinum crucible in the furnace, and the thermostat set in operation to hold the temperature constant. A platinum ball, whose volume had previously been determined by weighing it suspended in water, was lowered into the furnace chamber through a hole in the lid and weighed suspended above the glass. The ball was moved up and down several times after it had been immersed in the molten glass to remove bubbles of air which might cling to it. Before making a weighing, the suspension was adjusted so that the immersed ball was always the same distance above the bottom of the crucible holding the melt when the balance beam was in the "zero" position. There was no swing to the balance beam when the ball was immersed in the viscous glass. Weighings were made by placing suitable weights on the balance pan and noting where the beam came to rest. The weight was then varied by five milligrams and the new position of rest noted. The weight, to the nearest milligram, necessary to hold the suspension ball at the "zero" position was computed.

Densities were calculated from the loss of weight upon suspension and the volume of the ball (thermal expansion was taken into account), with correction for the effect of surface tension upon the suspending wire. At least two samples of each glass were used in finding densities at a number of different temperatures.

Sample Calculation

The following example has been presented to illustrate the method of calculation of surface tension from the experimental data:

*Maximum bubble-pressure method.

†Capillary rise method.

Data from observation of surface tension apparatus:

Manometer cm.	Readings cm.	Manometer Temp. deg. C.	Potentiometer Reading Millivolts	Tube Radius at 27 deg. C. cm.
11.38	3.85	31	11.70	0.0643

Additional data from tables, graphs, and calculations:

Manometer difference.....	7.53 cm.
Density of manometer liquid.....	1.037 gm. per ccm.
Value of "g" (Urbana).....	980.1 cm. per sec. per sec.
Thermocouple correction.....	0.09 millivolts
Temperature of glass.....	1186. deg. C.
Density of glass at 1186 deg. C.....	2.210 gm. per ccm.
Linear coefficient of thermal expansion of platinum tube.....	0.00001 cm. per cm. per deg. C.

If these values are substituted in the equation for calculating surface tension, the result is

$$T = \frac{7.53 \cdot 1.037 \cdot 980.1 \cdot 0.0643 [1 + 0.00001 \cdot (1186 - 27)]}{2}$$

$$\left\{ 1 - \frac{2}{3} \cdot \frac{0.0643 [1 + 0.00001 (1186 - 27)]}{\frac{7.53 \cdot 1.037}{2.210}} \right\}$$

$$= 248.1 \text{ dynes per cm.}$$

This is the value for surface tension which has been reported in the results of this investigation.

An additional correction which might have been applied arises from the tendency of the test liquid to exhibit capillarity in the containing vessel. Sugden* has shown the method of calculation from his table of corrections for surface tension values from the capillary rise in tubes.

The calculation of the correction involves the following symbols:

a = the so-called capillary constant—cm.

T = the surface tension—dynes per cm.

g = the gravity constant—cm. per sec. per sec.

D = the density of the test liquid—g. per cu. cm.

r = the radius of the vessel—cm.

h = the height of the capillary rise—cm.

b = a correction value to be obtained from Sugden's tables.

*Sugden, S. "The Determination of Surface Tension from the Rise in Capillary Tubes." Journ. Chem. Soc. Vol. 119, 1483, 1921.

If the values cited in the foregoing for the surface tension and the density of the glass are used, it is found that

$$a^2 = \frac{2T}{gD} = \frac{2 \cdot 248.1}{980 \cdot 2.21} = 0.229 \text{ sq. cm.}$$

The radius of the crucible at the liquid level was 1.75 cm.

$$a^2 = rh = 0.229$$

$$h = \frac{0.229}{1.75} = 0.131 \text{ cm.}$$

$$a = \sqrt{0.229} = 0.478 \text{ cm.}$$

$$\frac{r}{a} = \frac{1.75}{0.478} = 3.66$$

$$\frac{r}{b} = 0.077 \text{ (from Sugden's tables)}$$

$$b = 22.72$$

$$a^2 = bh = 0.229 = 22.7h$$

$$h = 0.010 \text{ cm.}$$

A column of glass, 0.010 cm. in height, would exert a pressure of

$$0.010 \times 980 \times 2.21 = 21.7 \text{ dynes per square cm.}$$

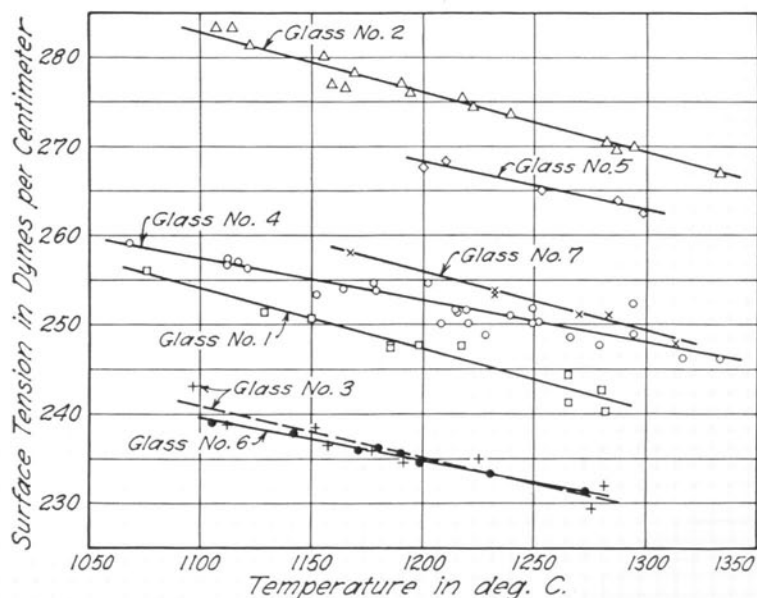
This pressure would influence the surface tension value to the amount of

$$\frac{21.7 (0.066)^2 \pi}{2\pi (0.066)} = 0.71 \text{ dynes per cm.}$$

(0.066 cm. was the approximate radius of the capillary tube.)

This correction is based on the assumption that the sides of the container were vertical (which they were not in the crucible used) and that the contact angle was zero. The effect of the tendency to rise along the outside of the capillary tube is neglected.

10. *Results.*—The results of the measurements of the surface tensions of the experimental glasses are presented graphically in Fig. 7. The equations showing the relation between surface tension

FIG. 7. SURFACE TENSIONS OF EXPERIMENTAL $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ GLASSESTABLE 3
SURFACE TENSIONS OF TEST GLASSES

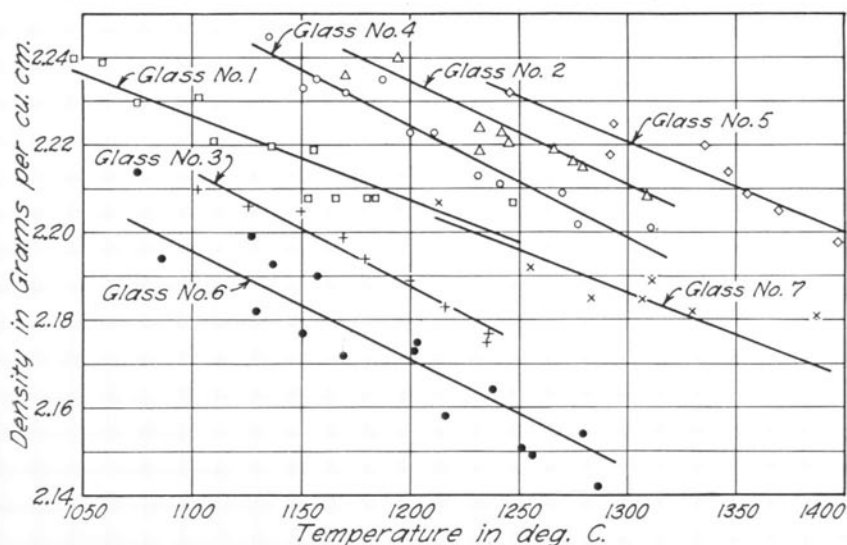
Glass No.	Surface Tension dynes per cm. at t deg. C.	Probable Error dynes per cm.
1	$328.9 - 0.0681t$	0.2
2	$356.7 - 0.0673t$	0.1
3	$304.7 - 0.0580t$	1.3
4	$308.4 - 0.0465t$	0.2
5	$334.0 - 0.0548t$	0.2
6	$292.6 - 0.0482t$	0.1
7	$336.3 - 0.0671t$	0.1

and temperature for these glasses were found* to be those shown in Table 3.

The results of the measurements of density are presented in the graph of Fig. 8. The equations representing the relation between density and temperature were found to be those shown in Table 4.

11. *Discussion of Results.*—The results of this investigation represent the surface tensions of the test glasses as lying between 230 and 290 dynes per centimeter in the temperature region of

*By method of least squares.

FIG. 8. DENSITIES OF EXPERIMENTAL $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ GLASSESTABLE 4
DENSITIES OF TEST GLASSES

Glass No.	Density grams per cc. at t deg. C.	Probable Error gram per cc.
1	$2.439 - 0.000193t$	0.001
2	$2.481 - 0.000208t$	0.001
3	$2.501 - 0.000261t$	0.001
4	$2.528 - 0.000253t$	0.001
5	$2.493 - 0.000210t$	0.001
6	$2.467 - 0.000247t$	0.001
7	$2.436 - 0.000192t$	0.001

1050-1350 deg. C.* The change of surface tensions of the test glasses with temperature is approximately the same, and probably could be considered as being the same, because of the similarity in the compositions.

The results, while differing considerably from those found by earlier investigators, fall in the range outlined by the investigation of Pietenpol and Scott. R. G. Hunter,[†] of Alton, Illinois, determined independently, by the ring method, the surface tension of one of the test glasses at a temperature of 1250 deg. C. with excellent agreement.

*The glasses were all heated to 1250 deg. C. before surface tensions were measured.

†Communicated.

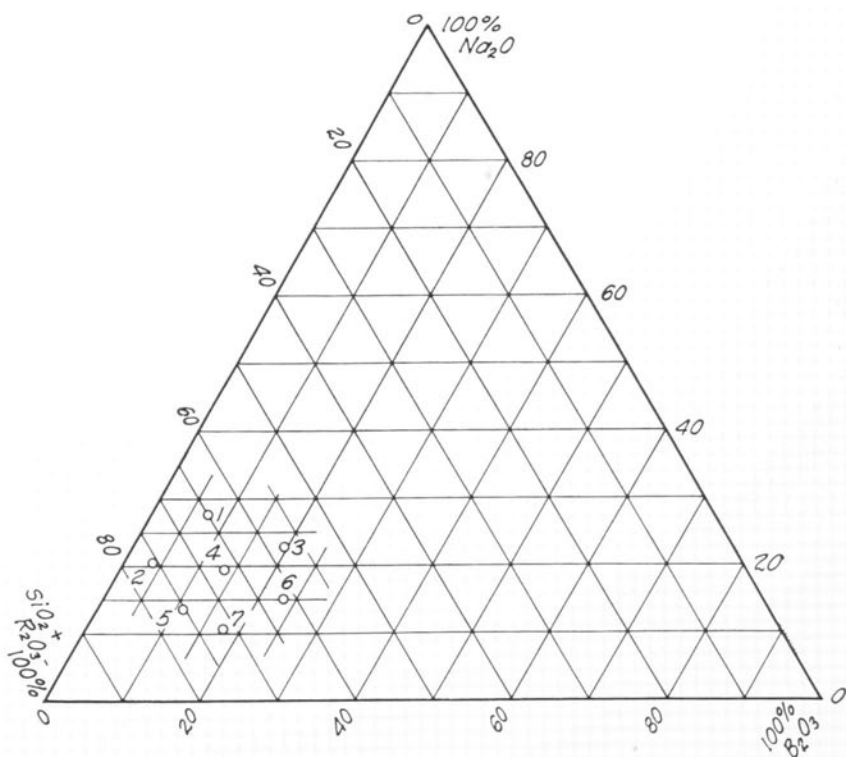


FIG. 9. APPROXIMATE COMPOSITIONS OF TEST GLASSES

The approximate compositions of the seven test glasses have been indicated in the composition diagram of Fig. 9. The R_2O_3 (chiefly Al_2O_3) was included with the SiO_2 because the results indicated that the addition of silica caused the surface tension of a glass to rise; and the work reported in the following section of this bulletin indicates that Al_2O_3 has the same effect. It must be remembered that the Al_2O_3 which was introduced into these glasses accidentally represents a minor portion in most cases.

Comparison of the diagram of Fig. 9 with that of Fig. 7 gives a clue to the effect of the composition of glasses of the type dealt with upon their surface tensions. Increase of SiO_2 (plus Al_2O_3) plainly increases the surface tension, as indicated by glasses numbered 5, 4, and 3. The general tendency is towards a decrease in surface tension with an increasing boric oxide content, as shown by comparison of glasses numbered 2, 4, and 6. An increase of Na_2O also has the effect of decreasing the surface tension. This is not so

readily shown on the diagram of Fig. 9, but may be visualized from glasses Nos. 1 and 5, also from Nos. 3 and 6 if it is realized that No. 3 must have an increase in B_2O_3 to properly demonstrate the effect of Na_2O changing and the ratio of SiO_2 to B_2O_3 remaining constant. This increase in B_2O_3 would put the surface tension of glass No. 3 fairly below that of No. 6. Boric oxide seems to have been more effective in lowering surface tension than was Na_2O .

It would seem that the surface tensions of the glasses in this system must be confined to a fairly definite range bounded on the lower side by the surface tension of Na_2O , B_2O_3 , or a combination of the two, and on the upper side by the surface tension of SiO_2 . The same limitations will be found generally with all silicate glasses.

The effects of the different component oxides upon the surface tension have further meaning in the light of the Gibbs* equation derived from thermodynamic considerations:

$$u = \frac{-c}{RT} \cdot \frac{d\gamma}{dc}$$

u = excess of any substance at the surface over c

c = concentration in the interior of the liquid

R = gas constant

T = temperature

γ = surface tension

$\frac{d\gamma}{dc}$ = change of surface tension with change of concentration.

It may be said that a sodium boro-silicate glass is richer in soda and boric oxide at the surface than in the interior of the glass when the findings of this investigation are interpreted in the light of Gibbs' equation. This observation may prove useful in explaining some of the phenomena relating to glass surfaces.

The determination of the densities of the test glasses was of secondary importance, and, while care was used in making the measurements, it is felt that the accuracy in some cases is not as great as the results would indicate. In general, it may be said that additions of SiO_2 increase the density, and that additions of Na_2O and B_2O_3 decrease the density. These statements refer particularly to density at higher temperatures.

NOTE

In heating the powdered glasses for testing, it was found that the surface tensions decreased with rising temperature from about 1100

*Gibbs, J. W., Trans. Conn. Acad., Vol. 3, 391, 1876.

to 1200 deg. C., as might be expected. From 1200 to 1250 deg. C. there was a rather sharp rise, which was followed by another fall comparable in slope to that preceding the 1200 deg. point. After some minutes at 1250 deg. C., the surface tension curve rose with falling temperature and did not revert to the values previously found for temperature below 1200 deg. C. The change which occurred at 1250 deg. C. seemed fairly stable. A similar change near 1400 deg. C. seemed rather steadily reversible. The causes of these changes were not found within the scope of the investigation.

III. CONCLUSION

12. *Conclusions.*—In conclusion, the authors feel that they have demonstrated the reliability of the maximum bubble-pressure method for use in measuring the surface tensions of molten glasses. They believe that the results which they have obtained very nearly express the absolute values of the surface tensions of the glasses tested.

The results of the investigation indicate that, within these limits:

(1) The addition of silica to a soda-boric oxide-silica glass causes a rise in the surface tension of the glass.

(2) The general tendency of the addition of soda or of boric oxide to a soda-boric oxide-silica glass is to reduce the surface tension.

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PART II

SURFACE TENSIONS OF SODA-LIME-SILICA MELTS

IV. INTRODUCTION

13. *Purpose and Scope of Investigation.*—The purpose of this investigation was the determination of the relation between surface tension, temperature, and composition for that part of the soda-lime-silica system which contains compositions of importance and interest to glass technologists. A sufficient number of compositions were studied to enable the construction of the surface tension-composition surface for an important part of the system.

14. *Previous Surface Tension Determinations of Soda-Lime-Silica Glasses.*—The surface tensions of melts in this system have been studied by Washburn and Libman.* They devised a dipping cylinder method for the purpose. The results reported by Washburn and Libman do not agree with those obtained by the maximum bubble pressure method.

V. METHOD AND PROCEDURE

15. *Method and Apparatus.*—The determinations were made by the maximum bubble pressure method using the apparatus described in Part I, slightly modified in a few details. The original capillary tube and adjusting head is shown in Fig. 2c. This was modified by replacing the short capillary tube with one 10 in. in length, which was connected to the air system by means of a flange and a packing nut. The rest of the apparatus was the same as that described in Part I, except that the parts of the apparatus were connected with copper tubing and that a pressure-regulating device was inserted between the manometer and the capillary. The pressure regulator consisted of rubber tubing partially filled with mercury which was connected into the air line between the furnace and the manometer. It was supported between this point and a movable head to form a flexible U-tube. The pressure on the system was varied by adjusting the movable supporting head upward or downward. A sketch of the improved apparatus is shown in Fig. 10.

*"The Viscosities and Surface Tensions of the Soda-Lime-Silica Glasses at High Temperatures," Univ. of Ill. Eng. Exp. Sta. Bul. 140, 1924.

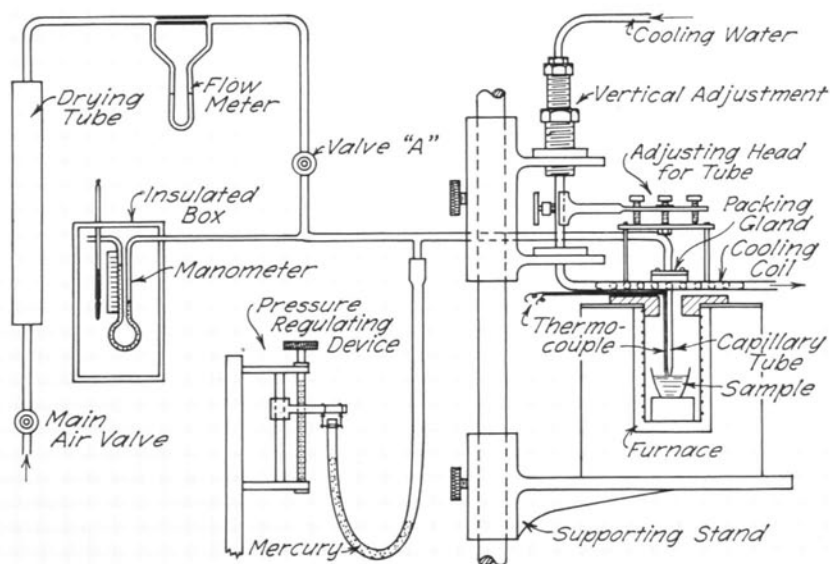


FIG. 10. SKETCH OF MODIFIED SURFACE TENSION APPARATUS

16. *Procedure.*—A platinum crucible containing the powdered sample was put in a small platinum resistance furnace, and the temperature raised to a maximum of 1350 to 1400 deg. C. This temperature was maintained for two or three hours to allow the furnace to attain equilibrium, and to allow the bubbles in the glass at that temperature to escape. While the furnace was heating, the diameter of the opening of the capillary tube was measured by means of a microscope. The tube was then mounted in its place over the furnace, and the furnace moved upward until the capillary tube was near the surface of the melt. A constant stream of air was kept flowing through the capillary to keep the liquid from backing up and clogging the platinum tube.

When the furnace and melt had reached a constant temperature of 1350 to 1400 deg. C., the capillary (with a constant stream of air flowing through it) was lowered carefully by turning the lowering screws until the static pressure in the air system began to increase. Valve A (Fig. 10) was then closed and opened. If air continued to flow, showing that the capillary had not made contact with the melt, the tube was again lowered slightly and valve A again closed and opened. This process was repeated until contact was made with the liquid as shown by the sharp rise of pressure when the valve

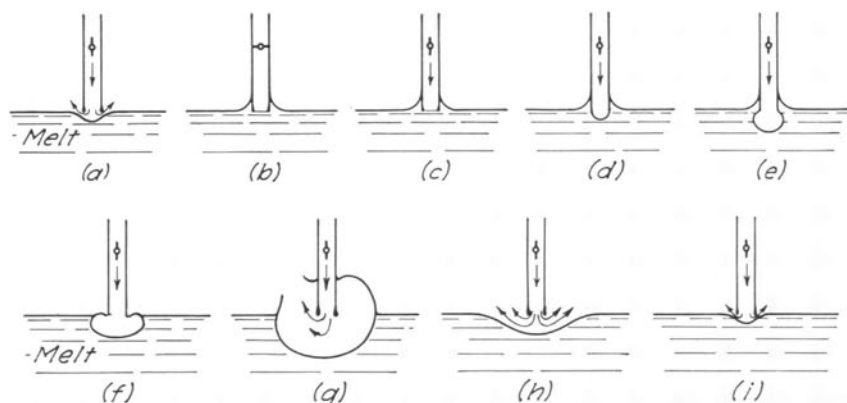


FIG. 11. SKETCHES SHOWING FORMATION AND BURSTING OF BUBBLES

was opened. The manometer liquid would rise to about 14 cm., then rapidly fall away to about one centimeter and remain there. The valve was again closed and opened, to form a new bubble, since the liquid level in the crucible was lowered somewhat as some of the melt was drawn from the crucible to coat the platinum capillary. In general this condition had reached equilibrium in about half an hour, when the final setting at that temperature could be made. The capillary tip and the melt now occupied the positions illustrated in *a*, Fig. 11. When valve *A* was closed the liquid flowed around the tube as shown in *b*, Fig. 11. If the valve was then opened, pressure was built up in the tube. Diagram *d*, Fig. 11, shows the condition when the stress in the surface of the bubble is a maximum. Upon further increase of pressure, the curvature of the bubble changes from spherical, and more air rushes in, expanding the bubble until it finally bursts. The size of the bubble as it bursts varies with the viscosity of the liquid. In very viscous liquids, as a glass at 1000 deg. C., the bubble increases to proportions as shown in *g*, Fig. 11; *h*, Fig. 11, shows the displaced liquid returning to equilibrium, and at *i* it has assumed the same position as shown in *a*, Fig. 11, the original position.

By careful manipulation it was possible to adjust the tip to within ± 0.005 cm. of the surface of the liquid.

After this setting was made, a reading for the maximum pressure on the bubble was obtained by stopping the pressure at some arbitrary value (less than the breaking pressure) and increasing it in 0.02 cm. increments at 5-minute intervals until the bubble failed.

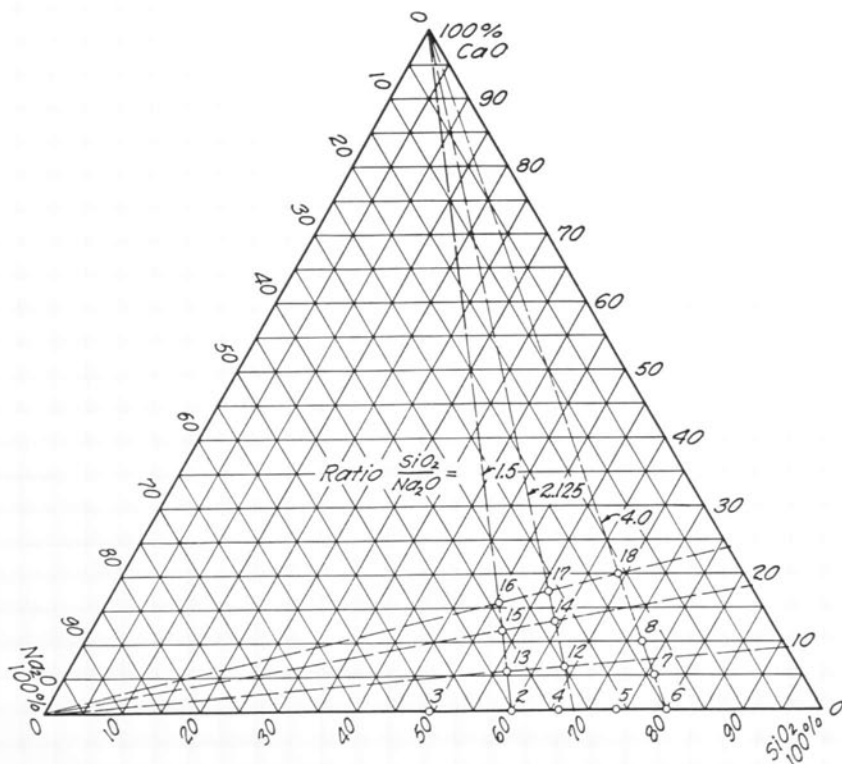


FIG. 12. RANGE OF COMPOSITIONS STUDIED

The procedure was then repeated by stopping the pressure at about 0.5 cm. below the breaking pressure, and maintaining that pressure for 15 minutes. This was to allow the manometer liquid to drain from the walls of the manometer tube, and to permit the attainment of equilibrium in the air system and in the viscous bubble. By means of the pressure regulator, the pressure was raised slowly to within about 0.10 cm. of the breaking pressure. From this point the pressure was increased in 0.02 or 0.01 cm. increments at 5-minute intervals until rupture occurred.

After the determination of values at a given temperature, the capillary was raised out of contact with the melt, and the sample caused to come to equilibrium at some lower temperature. The procedure described in the foregoing was then repeated. All other details of procedure were the same as described in Part I.

TABLE 5
CALCULATED PERCENTAGE COMPOSITIONS OF GLASSES
(Computed from batch)

No.	Na ₂ O	CaO	SiO ₂	$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$
2	40.0	60.0	1.50
3	50.79	49.21	0.97
4	34.04	65.96	1.94
5	26.40	73.60	2.79
6	20.00	80.00	4.00
7	19.00	5.00	76.00	4.00
8	18.00	10.00	72.00	4.00
11	37.8	62.20	1.64
12	30.00	6.25	63.75	2.13
13	37.85	5.55	56.61	1.50
14	27.85	13.04	59.11	2.13
15	35.32	11.69	52.99	1.50
16	33.68	15.79	50.53	1.50
17	26.38	17.53	56.09	2.13
18	16.00	20.00	64.00	4.00

VI. SURFACE TENSIONS OF SODA-LIME-SILICA GLASSES

17. *Compositions Studied.*—The field of compositions studied is shown in Fig. 12. The compositions of the experimental melts, as calculated from the batches, are given in Table 5.

18. *Preparation of Samples.*—The samples, prepared from pure reagent chemicals, in quantities corresponding to 33 grams of melted glass, were weighed on an analytical balance, transferred to wide-mouth bottles and mixed thoroughly by shaking each individual batch. They were then transferred to a platinum crucible and heated 12 hours at 1100 to 1150 deg. C.; the temperature was then raised to 1350 deg. C. for two hours, and the melt poured on platinum foil. The glass was crushed in a hardened steel diamond mortar to pass a 60-mesh silk lawn. The metallic iron accumulated from the crushing operations was removed with an electro-magnet. Samples were remelted at 1350 deg. C. for 5 hours and re-crushed. All samples were remelted four times. The powdered glass thus obtained was used immediately for surface tension measurements.

19. *Results.*—The experimental data for sample No. 5 are given in Table 6, and the surface tensions for all the melts are summarized in Table 7 and plotted in Fig. 13.

In all the calculations a value of 2.4 was used for the density of the melts. This seems quite satisfactory, as may be seen from Table 8, in which the surface tension values were computed from the same maximum bubble pressure by assuming different values for the

TABLE 6
EXPERIMENTAL RESULTS FOR GLASS NO. 5

Thermocouple Reading millivolts	Correction millivolts	Corrected Thermocouple Reading millivolts	Temperature deg. C.	Manometer Scale Reading-Zero Pressure, cm.	Manometer Scale Reading, cm.	Height of Manometer Liquid, h_m cm.	Temperature of Manometer deg. C.	Density of Manometer Liquid, d_m
14.50	0.17	14.67	1428	6.68	12.07	10.78	27.8	1.0399
14.50	0.17	14.67	1428	6.68	12.07	10.78	27.8	1.0399
13.67	0.13	13.80	1356	6.68	12.10	10.84	27.8	1.0399
13.67	0.13	13.80	1356	6.68	12.11	10.86	28.0	1.0397
13.45	0.12	13.57	1337	6.68	12.12	10.88	28.2	1.0395
13.45	0.12	13.57	1337	6.68	12.12	10.88	28.2	1.0395
13.35	0.12	13.47	1328	6.68	12.13	10.90	28.5	1.0393
13.35	0.12	13.47	1328	6.68	12.13	10.90	28.5	1.0393
12.45	0.10	12.55	1252	6.71	12.19	10.96	29.5	1.0384
12.44	0.10	12.54	1251	6.71	12.19	10.96	29.7	1.0383
12.44	0.10	12.54	1251	6.71	12.19	10.96	29.7	1.0383
11.70	0.08	11.78	1187	6.71	12.21	11.00	30.0	1.0380
11.57	0.08	11.65	1176	6.71	12.22	11.02	30.1	1.0379
11.30	0.08	11.38	1154	6.71	12.225	11.30	30.1	1.0379

TABLE 6
EXPERIMENTAL RESULTS FOR GLASS NO. 5 (CONCLUDED)

Manometer Pressure grams per cc. — P	Tube Diameter at Room Temperature cm.	Expansion of Tube cm.	Tube Diameter D at Furnace Temperature cm.	$h = \frac{d_m}{d} \times h_m$ glass	$\frac{2r}{3h}$	$1 - \frac{2r}{3h}$	PD grams	Surface Tension dynes per cm.
11.21	0.1008	0.0015	0.1023	4.67	0.0073	0.9927	1.147	276.0
11.21	0.1008	0.0015	0.1023	4.67	0.0073	0.9927	1.147	276.0
11.26	0.1008	0.0015	0.1023	4.69	0.0073	0.9927	1.152	277.2
11.29	0.1008	0.0015	0.1023	4.70	0.0073	0.9927	1.155	278.0
11.31	0.1008	0.0015	0.1023	4.71	0.0072	0.9928	1.157	278.3
11.31	0.1008	0.0015	0.1023	4.71	0.0072	0.9928	1.157	278.3
11.32	0.1008	0.0014	0.1022	4.71	0.0072	0.9928	1.157	278.3
11.32	0.1008	0.0014	0.1022	4.71	0.0072	0.9928	1.157	278.3
11.38	0.1008	0.0014	0.1022	4.74	0.0072	0.9928	1.163	280.0
11.38	0.1008	0.0014	0.1022	4.74	0.0072	0.9928	1.163	280.0
11.42	0.1008	0.0013	0.1021	4.76	0.0071	0.9929	1.167	280.9
11.43	0.1008	0.0013	0.1021	4.76	0.0071	0.9929	1.167	281.0
11.45	0.1008	0.0013	0.1021	4.77	0.0071	0.9929	1.169	281.3

TABLE 7
SURFACE TENSIONS OF GLASSES (CONTINUED)

Glass No. 11		Glass No. 12		Glass No. 13		Glass No. 14		Glass No. 15		Glass No. 16	
Temp. deg. C.	Surface Tension dynes per cm.	Temp. deg. C.	Surface Tension dynes per cm.	Temp. deg. C.	Surface Tension dynes per cm.	Temp. deg. C.	Surface Tension dynes per cm.	Temp. deg. C.	Surface Tension dynes per cm.	Temp. deg. C.	Surface Tension dynes per cm.
1358	281.3	1338	300.0	1353	295.7	1327	311.0	1370	311.7	1334	319.5
1327	284.2	1338	300.0	1353	295.7	1327	311.0	1370	312.2	1335	319.0
1327	284.2	1287	301.7	1353	295.7	1303	312.6	1337	312.4	1335	319.5
1263	286.9	1287	301.7	1273	301.1	1303	312.6	1337	312.4	1294	322.1
1263	286.4	1287	301.2	1273	301.4	1203	312.6	1337	312.9	1294	322.1
1263	286.9	1287	301.2	1237	302.9	1202	315.2	1306	313.4	1246	323.3
1263	286.4	1246	302.7	1237	302.9	1202	315.2	1306	313.4	1246	323.3
291.4	286.4	1246	302.2	1150	306.9	1280	317.8	1280	313.4	1188	323.2
1104	293.5	1214	302.4	1150	307.4	1140	317.8	1280	313.4	1188	323.2
1104	293.5	1358	297.7	1280	313.8	1176	326.5
1030	296.3	298.1	1280	313.8	1176	326.8
1030	296.3	1179	318.0
1030	296.3	1179	318.0

TABLE 7
SURFACE TENSIONS OF GLASSES (CONCLUDED)

Glass No. 17		Glass No. 18		Glass No. 2	
Temp. deg. C.	Surface Tension dynes per cm.	Temp. deg. C.	Surface Tension dynes per cm.	Temp. deg. C.	Surface Tension dynes per cm.
1355	321.4	1388	322.5	1375	290.5
1355	321.9	1388	322.5	1375	290.5
1355	321.9	1388	323.0	1375	290.5
1279	323.1	1280	323.7	1302	290.7
1279	323.5	1280	323.7	1302	291.2
1279	323.1	1214	324.4	1215	292.8
1238	324.7	1214	324.4	1215	292.8
1238	324.7	1132	295.1
1238	324.7	1132	295.1

densities of the glass. It appears that the error due to the assumption of a density of 2.4 for all melts at all temperatures is within the probable error of the experiment.

20. *Temperature Coefficients of Surface Tension.*—The mean temperature coefficients $\left(\frac{\Delta T}{\Delta t}\right)$ between 1200 and 1350 deg. C.

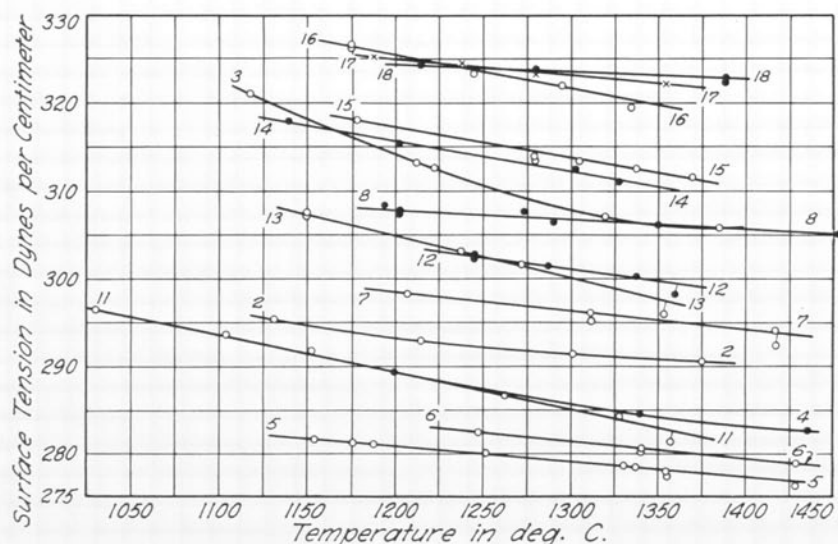


FIG. 13. VARIATIONS OF SURFACE TENSIONS OF $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ GLASSES WITH TEMPERATURE

TABLE 8
EFFECT OF DENSITY ON COMPUTED SURFACE TENSION

$\frac{Pr}{2}$	$\frac{2r}{3h}$	Density of Glass	Surface Tension
0.3171	0.00855	2.0	308.2
0.3171	0.01025	2.4	307.8
0.3171	0.01200	2.8	307.2

were determined from the curves in Fig. 13. These coefficients are shown in Fig. 14 plotted as ordinates against the ratio of the percentages of SiO_2 to Na_2O as abscissas. The data for 13 melts have been plotted, and the approximate percentage of CaO in each sample indicated near each plotted point. Mean curves have been drawn through points of constant CaO . A sufficient number of points were available to enable the construction of a curve for zero per cent CaO and the dispersion was small. The position of the curve labeled "15 per cent CaO " shows that the addition of CaO to a Na_2O - SiO_2 melt lowers the temperature coefficient of surface tension, but the

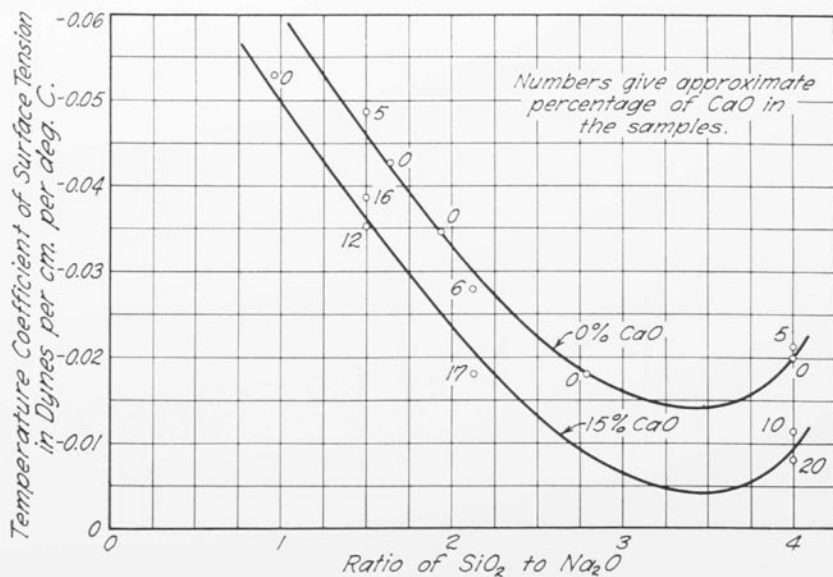


FIG. 14. RELATION BETWEEN TEMPERATURE COEFFICIENTS OF SURFACE TENSIONS OF Na_2O - CaO - SiO_2 MELTS AND THEIR COMPOSITIONS

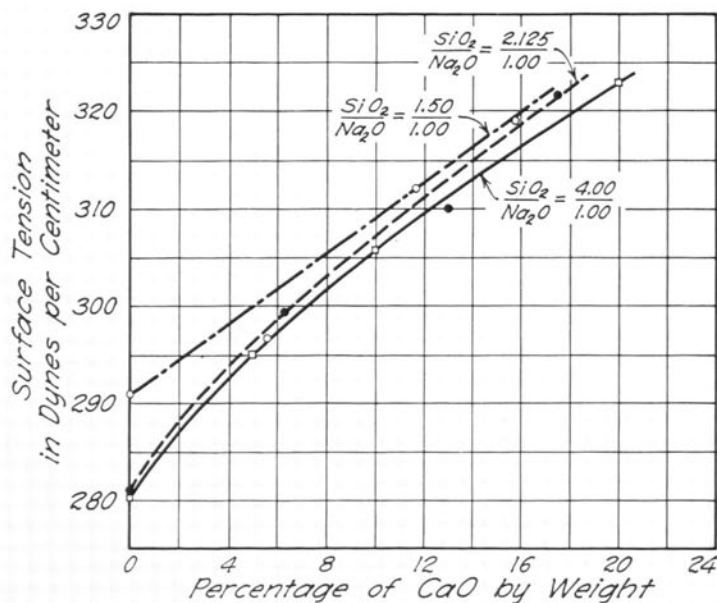


FIG. 15. EFFECT OF CaO ON SURFACE TENSION OF $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ MELTS AT 1350°C .

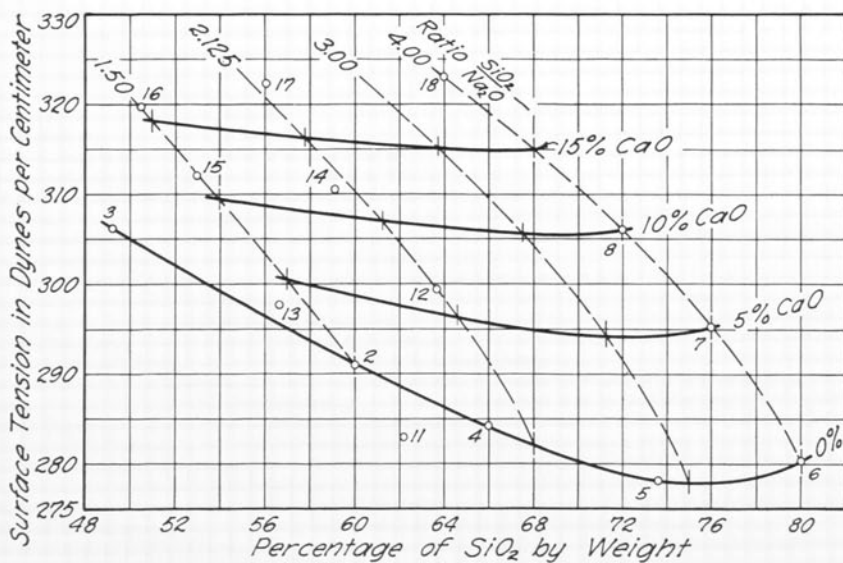


FIG. 16. SURFACE TENSIONS OF $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ MELTS WITH CONSTANT CaO AT 1350°C .

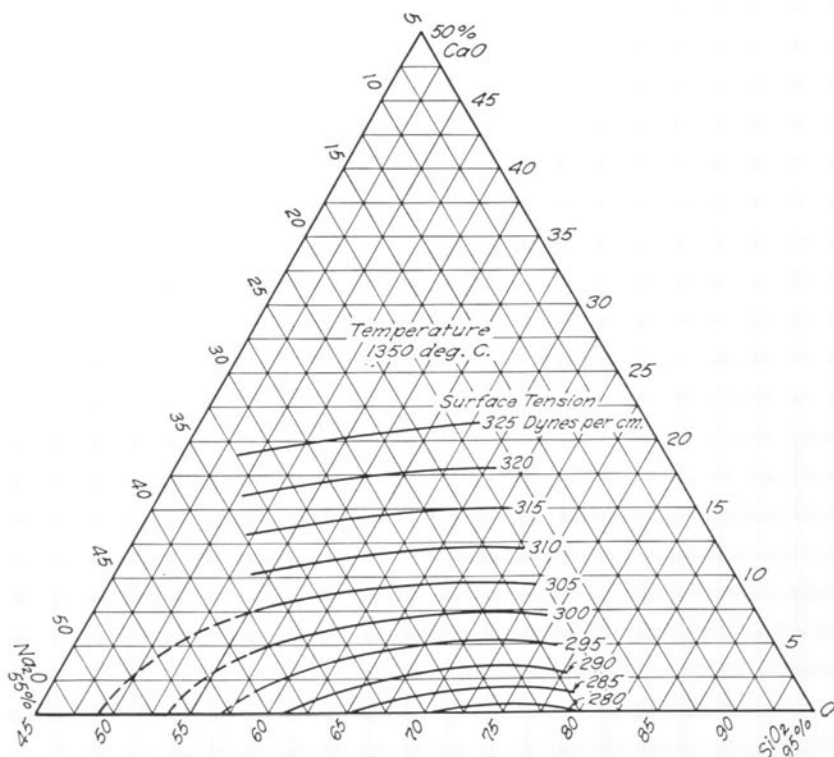


FIG. 17. SURFACE TENSIONS OF $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ SYSTEM AT CONSTANT TEMPERATURE

effect is not great. The value of $-\left(\frac{\Delta T}{\Delta t}\right)$ reaches a minimum at a $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio (ratio of their weight percentages) of about 3.5. A similar minimum was found for the surface tension curves.

21. *Relation Between Surface Tension and Composition.*—The relation between surface tension and composition is shown in Figs. 15, 16, and 17. The effect of CaO on surface tension is best shown in Fig. 15. Each curve represents variable CaO with constant $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio. Each curve has a different slope, the intermediate $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio curve has the intermediate slope.

Figure 16 has been plotted from data obtained by interpolation from Fig. 15, in order to obtain a clear picture of the effect of Na_2O and SiO_2 on the surface tensions. The percentage of silica was arbitrarily chosen as the abscissa. The percentage of Na_2O at any

point may be obtained by subtracting the sum of the lime and silica from 100.

These curves show the existence of a minimum surface tension at a $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of about 3, for zero CaO , the minimum shifting toward higher ratios with increasing lime. Similar minima were noted for the temperature coefficients. The most stable glasses occur to the right of the minima.

The contour lines in Fig. 17 are the loci of compositions having the same surface tension at 1350 deg. C. Composition is represented as weight per cent. These curves are drawn by interpolation from Figs. 15 and 16.

The relation between surface tension and composition is rather simple over a wide range of compositions. The surface tension is influenced greatly by CaO , but only slightly by Na_2O and SiO_2 , except for very high values of Na_2O .

22. *Relation Between Surface Tension and Viscosity.*—Some of the melts behaved in an exceptional manner when poured. While attempting to transfer the melts of samples Nos. 15, 16, and 17, the liquids seemed to drip from the crucible rather than to pour. The action was suggestive of the behavior of mercury when being emptied from a vessel. When these molten silicates were poured on platinum foil they had a strong tendency to form in spherical masses. This caused the liquid to roll about on the platinum foil rather freely. It was almost impossible to draw a thread of glass from these particular melts, due to the extreme tendency of the melts to form globules or beads.

These phenomena were indicative of very high surface tension, but other melts of different composition, with surface tensions as high or higher, have quite normal working properties. In the first case the viscosity was low, while in the latter case both the surface tension and viscosity were high. If the liquid has a high surface tension and a low viscosity, the forces of surface tension greatly influence the manner of flow.

In a general way the relation between viscosity and surface tension in the Na_2O - CaO - SiO_2 system is rather simple. At least that is true of the part of the field investigated, as is shown in Fig. 18. In this illustration the viscosity-composition curves have been superimposed upon a plot of the surface tension-composition curves. The values of viscosity were taken from Washburn and Shelton.* Lines of constant viscosity are in general parallel to the lines of

*Univ. of Ill. Eng. Exp. Sta. Bull. 140, 1924.

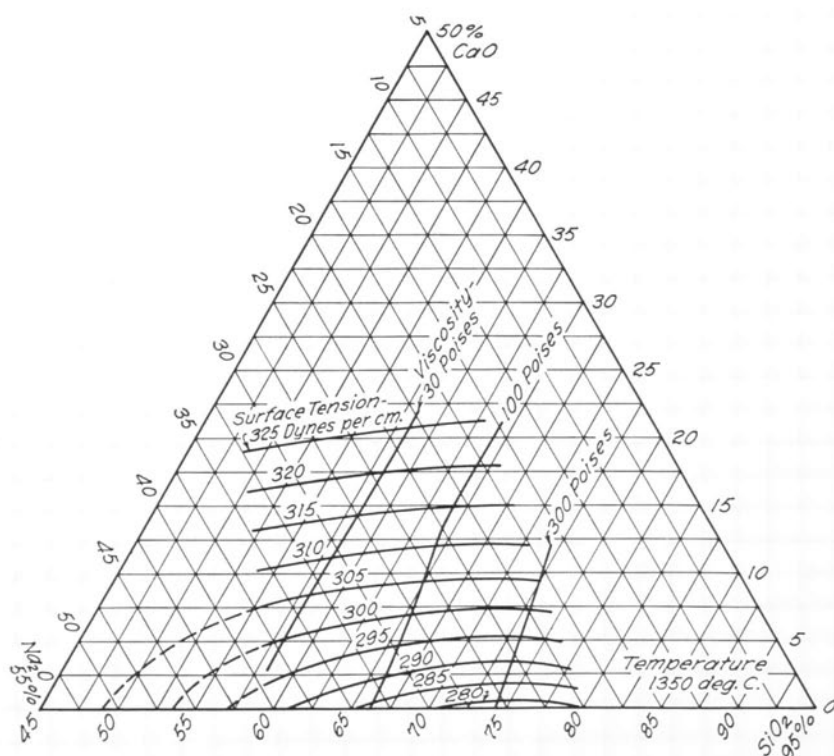


FIG. 18. RELATION BETWEEN SURFACE TENSION AND VISCOSITY
IN $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ SYSTEM

constant silica, while the equi-surface-tension lines tend to parallel the lines of constant CaO .

VII. DISCUSSION OF RESULTS

23. *Accuracy and Precision of Results.*—The results have been summarized in Table 7 and in Figs. 13 to 17. The points obtained for each glass fall very close to a smooth curve. These curves show that the degree of precision, as regards the determinations on any given melt, was satisfactory. The highest degree of precision was obtained with melts of the lowest viscosity. Reference to Fig. 15 shows that values of surface tension for a single temperature but for varying composition, with but two exceptions, fall on smooth curves. Since the temperature coefficients of these two glasses, as well as their surface tensions, were not in close agreement with the other

data, it was assumed that the error was in the composition of the glasses. Each of these points is 3 dynes from the curve, which represents an error of about one per cent. In previous work on surface tension this type of error has been encountered on rare occasions. In every case the error was eliminated by repeat determinations on a new batch of glass.

24. *Comparison of Results With Those of Previous Investigators.*—The work of previous investigators has been reviewed in Section 3 of Part I. The values reported here are not in accord with those found in the earlier literature, with the possible exception of the values reported by Griffith* and by Pietenpol.† Pietenpol's values for commercial glasses at temperatures of 550 to 900 deg. C. were 230 to 360 dynes per cm. These values are about the same order of magnitude as those reported in the present paper. Griffith measured the surface tension of a glass of the following composition: SiO_2 , 69.2 per cent; Na_2O , 0.9 per cent; Al_2O_3 , 11.8 per cent; CaO , 4.5 per cent; MnO , 0.9 per cent; K_2O , 12.0 per cent. Measurements were made of the sag of small fibers between 730 and 900 deg. C. The surface tension was found to be 418 dynes per centimeter at 905 deg. C. For a specimen of that composition and at that temperature, the value is considered to be in essential agreement with those determined by the maximum bubble pressure method.

Quite recently G. Keppeler‡ has published the results obtained in the surface tension measurement of six glass compositions containing boric oxide, using the maximum bubble pressure method. These data are of the same order of magnitude as reported in this paper.

VIII. SUMMARY

25. *Scope of Investigation.*—The surface tensions of melts in the soda-lime-silica system were determined. Fourteen compositions were studied which varied from zero to 20 per cent CaO , from 50 to 80 per cent SiO_2 , and from 16 to 40 per cent Na_2O . The SiO_2 : Na_2O ratios varied from 1.5 to 4. The maximum temperature of any observation was 1456 deg. C. and the minimum temperature was 1030 deg. C. Important details regarding the method and technique have been discussed.

*Griffith, A. A., loc. cit.

†Pietenpol, W. B., and Scott, H. H., loc. cit.

‡Keppeler, G., The Surface Tension of Glass, Trans. Soc. of Glass Technology, Vol. 21, p. 53, 1937.

26. *Data Reported.*—The surface tensions of a wide range of melts in the Na_2O - CaO - SiO_2 system have been reported. Data regarding the temperature coefficients of surface tension as a function of composition have been presented.

IX. CONCLUSIONS

27. *Conclusions.*—The following conclusions are offered:

(1) The surface tensions of soda-silica and soda-lime-silica melts are increased rapidly by the addition of calcium oxide. At 1350 deg. C., this increase amounts to between 3.0 and 1.8 dynes per centimeter for each per cent of CaO added.

(2) The surface tensions of soda-silica melts have a minimum value at about 72 per cent silica at 1350 deg. C. The surface tension increases about 1 dyne per centimeter for each per cent decrease in silica from 72 per cent, or each per cent Na_2O . An increase in silica from 72 to 80 per cent raises the surface tension from 278 to 280.5 dynes per centimeter.

(3) The addition of CaO to soda-silica melts decreases the effect of Na_2O and SiO_2 on surface tension. The minimum point moves to lower $\text{SiO}_2 : \text{Na}_2\text{O}$ ratios with increasing CaO , and is apparently absent at about 15 per cent CaO . Melts with 15 per cent CaO show an increase in surface tension from 3.5 dynes per centimeter at 68 per cent silica to 3.8 dynes per centimeter at 51 per cent silica.

(4) The surface tension is nearly proportional to the CaO content, while curves of constant viscosity tend to parallel lines of constant SiO_2 .

(5) The temperature coefficient of surface tension is reduced by the addition of CaO . The value of $-\frac{T}{t}$ reaches a minimum at a $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of about 3.5.

(6) The tests made have yielded data which have been checked in some cases in other laboratories, using glasses of the same or similar compositions. The method has yielded consistent results on samples of glasses of like composition made under commercial conditions. It seems probable that the same or similar glasses will give similar results irrespective of the time-temperature conditions of melting providing that these do not vary too widely. Due attention should be paid to the time factor to eliminate the effects of the forces of viscosity.

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2. Background

3. Methodology

4. Results

5. Discussion

6. Conclusion

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14. Data Availability Statement

15. Supplemental Material

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